ON REVISING THE WATER QUALITY CRITERIA FOR AMMONIUM IN COASTAL WATERS
- TECHNICAL REPORT –
Department of Health, Environmental Planning Office
July, 2002

Introduction:

Several large data sets containing measurements of salinity, silicates and ammonium in coastal water samples collected between September, 1989 and November, 1999 now provide sufficient statewide coverage to support amendment of the coastal water quality criteria for ammonium listed in the Hawaii Administrative Rules, Chapter 11-54, Water Quality Standards. The existing ammonium criteria for coastal waters, promulgated in 1979 and compiled in the current rule in §11-54-06(b)(3), were developed from limited data collected from a small number of locations and averaged across sampling sites. Because samples were originally collected from small boats, and because sample collection today is often accomplished by wading out from shore as well as by collecting samples from vessels in deeper water, ammonium water quality standards (WQS) are needed that take both shoreline and deeper coastal water conditions into account.

Under the antidegradation requirements of the federal Clean Water Act (33 U.S.C. §1251-1387, ELR Stat. FWPCA §101-607), these criteria have been retained in the absence of enough data from waters relatively free from human-related sources of pollution to support additional analyses. These data are now available, and have been analyzed on a site-specific basis rather than averaged in order to develop new criteria for ammonium in coastal waters that, for the first time, explicitly account for the impact of coastal groundwater discharges on nearshore water quality. The State Water Quality Standards for coastal waters generally apply to the well-mixed and well-lit upper 30.5 m (100 feet) of the water column extending from the shoreline to the 183 m (600 foot) depth contour; the sample spaces described below conform to these boundaries.

Because ammonium is both introduced into coastal waters from land and regenerated by biological activity in the water column and on the seafloor, this parameter is highly variable in space and time, not present in significant onshore-offshore concentration gradients, and requires large data sets for evaluation. The amendment proposed below, based on a total of 4,585 data points collected from 28 locations across the State, increases the existing ammonium concentration criteria for open coastal waters from 2.00 micrograms/L for “dry” coastal conditions and 3.50 micrograms/L for “wet” coastal conditions to either 4.00 micrograms/L or 8.00 micrograms/L as a function of salinity and silicate concentrations in the area of interest. “Dry” and “wet” coastal conditions refer to estimates, often highly uncertain, of the volume of freshwater discharged into nearshore coastal waters as less than (“dry”) or more than (“wet”) three million mgd per shoreline mile. The proposed amendment replaces the “dry” and “wet” estimates with two salinity categories, and replaces the “fifty, ten or two ten per cent of the time” ammonium criteria with single concentration criteria corresponding to each of two salinity categories, “lower” (greater than 32.000 ppt and less than or equal to 34.400 ppt) and “higher” (greater than 34.400 ppt), to be defined by measurement within the area of interest. Silicate measurements are used together with salinity to identify the relative magnitude of groundwater inputs and to select the appropriate ammonium criteria for the area of interest. Ammonium and silicate concentrations are reported as geometric means, and corresponding salinities are reported as arithmetic means throughout this document.

These proposals reduce uncertainty and simplify the ammonium criteria by replacing the wet/dry criteria and the corresponding three geometric mean criteria with a requirement for measurement of salinity and silicates, followed by selection of a single corresponding ammonium criterion for an area. Costs may be initially higher as the salinity/silicate profiles of different sections of coastal waters are measured, but these measurements need only be made once , unless a significant change in adjacent land uses that includes changes in drainage patterns warrants another round of sampling. Cost savings will also be realized by no longer requiring analysis of freshwater discharge volumes along the shoreline to determine if the area meets "dry" or "wet" criteria. Although the current proposal applies only to the ammonium criteria for coastal waters, similar analyses will be conducted on other water quality parameters as data become available from both leeward and, especially, the wetter, windward sides of the major islands where discharges from perennial stream systems affect concentrations of oxidized forms of nutrients, such as nitrate and phosphate.

In order to clarify the existing definition of "open coastal waters" for permit-writing purposes, we are also proposing to restrict the definition to waters of salinity greater than 32.000 ppt. Waters of lower salinity will be defined as brackish, even if they are in coastal areas, and should be evaluated using the table of numeric criteria for estuaries [§11-54-05.2(d)(1)]. Salinity, silicate and ammonium data were deleted before analysis from the data sets reported on below if the measured sample salinity was less than or equal to 32.000 ppt, a concentration which corresponds to a fresh water content of less than 10 per cent. The lower boundary for open ocean salinities is about 34.400 ppt; as estimated from UH/HOT data collected at station ALOHA 2 located at 22.75 N, 158 W, about 100 km northeast of Oahu; data reported at http://hahana.soest.hawaii.edu/hot/hot-dogs/interface.html;; see Figure 1). Silicates, which dissolve from rocks exposed to fresh water flows on land, are also useful as a tracer of surface water and groundwater discharges into the coastal ocean, and are often used in combination with salinity to evaluate impacts of fresh water discharges on coastal water quality (Laws & Ziemann, 1995).

Descriptions of Data Sets:

Three investigators from the University of Hawaii at Manoa contributed data to the proposed amendment – Dr. Richard Brock, Dr. Steven Dollar, and Dr. Edward Laws. Water samples were analyzed at the Analytical Services Laboratory, School of Ocean & Earth Science & Technology, University of Hawaii.

DETECTION LIMITS	ACCURACY
Ammonium: 0.4 micrograms/L Silicate: 5.6 micrograms/L Salinity: 0.0001 ppt	1.1 micrograms/L 14.0 micrograms/L 0.003 ppt

Measurements rarely fell below the detection limits; values reported as "ND" were replaced by the corresponding detection limit for the analysis. Ammonium and silicate data were transformed to natural logs prior to analysis; because the salinity range was restricted to a very narrow range of salinities greater than 32.000 ppt these data were not transformed. Although different locations had greatly different sample sizes, geometric means were assigned equal weights and compared across locations in order to preserve the effects of geographic variation in the results. Otherwise, overall means for lumped data would have been disproportionately influenced by the largest data sets, Ewa Marina (Dollar) and Lanai (Brock). Raw data tables are available electronically by request.

1. **Data collected by Brock**. These data are from a ten-year data collection effort spanning the years from September, 1989 to November, 1999. The data include measurements of ammonium (n = 1,496), silicate (n = 1,444) and salinity (n = 1,496) from 14 locations statewide (Table 1; Figure 5). Most water samples were collected within 1000 m from shore (71%) and from depths less than 24.4m (98%). Three locations were *a priori* excluded from the analysis – Sand Island, Maui Electric Co. and Barbers Point because they are adjacent to discharges of treated sewage effluents; one location (Honokohau Harbor, island of Hawaii) was excluded on the basis of unusual site characteristics (the harbor is a long, narrow artificial indentation in the coastline that is not typical of natural coastal features).

   Brock's data set is further characterized by assignment of sample sites as either "developed" or "undeveloped", based on the adjacent land uses. "Developed" coastlines are characterized by housing, golf courses, hotels, and commercial enterprises close to the shoreline. These developments range from relatively low density settings, such as the single golf course and hotel at Hulopoe Bay, Lanai, to dense urban areas along Honolulu's south shore, with a population in excess of 630,000. "Undeveloped" coastlines do not have buildings and golf courses directly fronting the shoreline, but may have roads and low density rural land uses well inland from the coast.

2. **Data collected by Dollar**. Dollar collected data near the surface and near the bottom along onshore-offshore transects starting at the shoreline and extending offshore to either 1000 m (West Hawaii) or 500 m (West Maui, Ewa Marina). Dollar's sample space for the West Hawaii and West Maui data was reduced in size for this analysis by including only samples from the upper 30.5 m of the water column and samples collected more than 2 m offshore in order to eliminate frequent low salinity samples collected closer to shore where mixing of fresh and marine waters is incomplete. For West Hawaii, n = 166 water samples from five coastal transects were collected between 02/94 and 06/95; for West Maui, n = 201 samples from five coastal transects were collected between 01/93 and 06/94; for Ewa Marina (Ocean Pointe), n = 2,940 samples from four coastal transects were collected from 06/90 to 06/00 (Table 1; Figures 7, 8). Samples from the Ewa Marina transects were representative of well-mixed conditions (salinities >32.000 ppt) up to the shoreline; no shoreline samples were deleted.

3. **Data Collected by Laws**. From 08/93 to 07/94, Laws collected one water sample per month about 2 m offshore at each of ten moderately- to-highly frequented public beaches along the south coast of Oahu (Laws & Ziemann, 1995). The presence of densely populated areas stretching from Diamond Head to Barbers Point strongly suggests that waters close to the shoreline are impacted by polluted runoff. Consequently, these data were not used to compute the revised criteria, but to evaluate the capacity of the new criteria to identify locations where anthropogenic impacts are affecting ammonium concentrations. These shoreline data were compared to data collected at 1 or 2 m from shore along less developed

coastal areas in West Maui and West Hawaii (Brock; Dollar), and at the proposed Ewa Marina development site (Dollar) (Table 2; Figure 6).

Results and Discussion:

Although data were included in the analysis only when the sample salinity was greater than 32.000 ppt, geometric means for both silicate and ammonium vary widely across locations (Table 1; Figure 2). In the open ocean around the Hawaiian islands salinities are rarely less than 34.4 ppt, the median silicate concentration is about 43 micrograms/L, and the median ammonium concentration is about 0.8 micrograms/L (ALOHA Station 2; Laws & Ziemann, 1995). Close to the coastlines a patchwork of areas with lower salinity and higher silicate values identify locations where surface water and groundwater discharges enter the coastal ocean and eventually mix to background levels in the downcurrent direction. In natural waters, defined as waters relatively unimpacted by human activities, elevated ammonium values are mostly associated with groundwater discharges; ammonium in fresh water surface flows oxidizes rapidly to nitrate (Laws & Ziemann, 1995).

Of the 28 locations sampled by Brock and Dollar, 11 were on the west side of the island of Hawaii, 7 on the west side of Maui, 6 on the south side of Oahu, and 2 on the east side of Kauai. Two sets of stations, the “undeveloped” and “developed” station groups, were sampled on the east and south shores of Lanai. In the geologically-young West Hawaii region rain falling mostly on high elevation volcanic slopes seeps into the porous lavas and moves seaward in shallow groundwater flows, discharging in large and persistent seeps at or near the coastline. West Hawaii, as yet relatively undeveloped and with no perennial surface streams contributing silicates and nitrates to nearshore waters, is a representative region for evaluating impacts of natural groundwater discharges on coastal water quality. These sites also represent the maximum likely natural concentrations of ammonium and silicate in Hawaiian coastal waters, as consolidation over geological time of materials in lava flows and development of caprock on the older islands has resulted in decreased rates of groundwater transport and discharge relative to that seen along the West Hawaii coastline (Gingerich and Oki, 2000). Coastal waters around the relatively undeveloped, low-rainfall island of Lanai represent the opposite end of the salinity/silicate/ammonium spectrum, with parameter concentrations closer to those in the offshore ocean.

When the 28 locations for which data are available for the ammonium analysis are ranked in order of salinity, the 13 sites with mean salinities less than the offshore lower bound of about 34.400 ppt had an overall mean ammonium concentration of 3.44 ± 1.70 micrograms/L and a corresponding mean silicate concentration of 258.96 ± 110.36 micrograms/L (Table 1). These 13 locations are assigned to the “lower salinity category” where mean salinity ranges from >32.000 ppt to ≤34.400 ppt. Nine of these locations are along the West Hawaii coastline.

For locations with salinities >34.400 ppt, mean ammonium concentrations were 1.86 ± 0.65 micrograms/L and mean silicate concentrations were 105.14 ± 45.18 micrograms/L (Table 1).

These mean salinity and silicate concentrations are correlated across locations at r = -0.76, with silicate values declining to a level equivalent to those in the offshore ocean (about 43 micrograms/L) at a salinity of about 34.800 ppt (Figure 3). Variability in mean silicate concentrations increased at salinities less than 34.000 ppt, reflecting the impact of groundwater discharges of variable volumes along the West Hawaii coastline. A multiple r equal to +0.60, or $r^2 = 0.36$, represents the correlation (low) among mean ammonium, silicate, and salinity values across all locations sampled.

Derivation of Two Proposed New Ammonium Criteria for Open Coastal Waters:

The uneven distribution of large groundwater discharges results in areas of contrasting water quality along the West Hawaii coastline, with very low mean ammonium concentrations detected at Honokua Gulch (0.71 micrograms/L; undeveloped site), compared to very high concentrations at Kukio (5.69 micrograms/L; also an undeveloped site at the time of sampling). The range of ammonium concentrations along West Hawaii includes most of the geometric mean concentrations measured on the other islands, and is wide enough to support development of two criteria for ammonium, one for each of two salinity categories.

Some developed sites (urban, residential, and agricultural lands) may not consistently meet the proposed criteria because of the presence of effluents from coastal cesspools or nutrient subsidies from commercial fertilizers. Over time, improved management of nonpoint sources of pollution is expected to result in improvement of water quality such that the new criteria will be met in all coastal waters. Developments proposed for areas adjacent to coastal waters not meeting the proposed criteria because of polluted runoff or polluted groundwater discharges may be subject to BMP requirements to reduce land use impacts; waters found to be impaired by high ammonium concentrations resulting from adjacent land uses are also subject to listing under CWA 303(d) followed by preparation of TMDLs for ammonium.

1. **Criterion for lower salinity category:**
   The maximum ammonium mean value among the 13 locations in the lower salinity category (between >32.000 ppt and ≤34.400 ppt) is 6.11 micrograms/L at Hanamaulu, Kauai, a developed site likely to be impacted by runoff and groundwater discharges associated with human land use activities. The next highest mean, however, is 5.69 micrograms/L ammonium from Kukio, a site in West Hawaii that was undeveloped at the time of data collection, and is at present subject to a housing development. Assuming that the water samples originally collected at the Kukio site contained close to the maximum natural background values of ammonium to be expected (coastal waters off Kukio are in Class AA) and using the analytical accuracy for ammonium reported by the SOEST lab (1.1 micrograms/L), we can assume that the true value of the mean ammonium concentration at Kukio may be as high as the upper 95% confidence limit on the mean, 6.64 micrograms/L, plus the estimated measurement error, or 6.64 micrograms/L + 1.1 micrograms/L = 7.74 micrograms/L, which for practical purposes, may be rounded off to 8.00 micrograms/L. Corresponding silicate values from these locations range from 155.55 micrograms/L on Kauai to 520.86 micrograms/L at Kaloko, island of Hawaii.

The proposed criterion of 8.00 micrograms/L, derived from the Kuhio data, is exceeded by 35 per cent of the measured ammonium concentrations at five undeveloped locations on the West Hawaii coastline that fall in the lower salinity category, but overall sample means meet the criterion. A geometric mean criterion equal to 8.00 micrograms/L will be adequate for all locations relatively unimpacted by human land use activities that meet the salinity criterion for this category, provided that the sample size and area sampled are large enough to incorporate the range of variability of ammonium, the most variable WQS parameter, at the site.

2. **Criterion for higher salinity category**.

The maximum ammonium mean value for undeveloped locations in the higher salinity category (n = 15 locations, salinity > 34.400 ppt) is equal to 2.40 micrograms/L ammonium at Mahukona, West Hawaii. The largest set of samples from undeveloped high salinity sites was collected on the island of Lanai; the overall geometric mean value equals 2.31 micrograms/L (n = 220). Assuming that water samples collected at the Mahukona and Lanai sites reflected the maximum natural background values of ammonium to be expected in the higher salinity waters (both Mahukona and Lanai have Class AA coastal waters), and using the analytical accuracy for ammonium reported by the SOEST lab (1.1 micrograms/L), we can assume that the true value of the mean ammonium concentration at the Mahukona and Lanai sites may be as high as the upper 95% confidence limit on the mean, 3.07 micrograms/L, plus the estimated measurement error, or 3.07 micrograms/L + 1.1 micrograms/L = 4.17 micrograms/L and 2.74 micrograms/L + 1.1 micrograms/L = 3.84 micrograms/L, respectively, which, for practical purposes, may be averaged to 4.00 micrograms/L. The proposed criterion of 4.00 micrograms/L, derived from the Mahukona and Lanai (undeveloped) data sets, is close to the existing “wet” criterion for ammonium in open coastal waters in the current rule (3.50 micrograms/L.) Silicate values from locations in the higher salinity category range from 40.49 micrograms/L on Oahu (the 100-foot hole site off the south shore) to 209.61 micrograms/L at the Ewa Marina (Ocean Pointe) control transect, south coast of the island of Oahu.

The proposed value of 4.00 micrograms/L is exceeded by 38 % of the measured ammonium concentrations at the two undeveloped locations included in the higher salinity category stations on the island of Lanai and at Mahukona, West Hawaii, but overall sample means are less than the criterion. A geometric mean criterion equal to 4.00 micrograms/L should be adequate for all locations that meet the salinity criteria for this category, provided that the sample size and area sampled are large enough to incorporate the range of variability of ammonium, the most variable WQS parameter, at the site.

Please note that the silicate ranges described for each of the two salinity categories overlap; silicate concentrations are typically but not always <150 micrograms/L for the lower salinity category and >210 micrograms/L for the higher salinity category. In general, the higher salinity category has lower corresponding silicate concentrations, but a clear demarcation of silicate values is not possible. The salinity categories should be used as the primary guides to use of the 8.00 micrograms/L or 4.00 micrograms/L WQS.

In cases where the mean salinity is at or very near 34.400 ppt and the choice of the appropriate ammonium criterion is ambiguous, silicate concentrations can be used as a "tiebreaker" to make the final decision. If silicate concentrations are low (<200 micrograms/L), as is characteristic of higher salinity waters, then the ammonium criterion at 4.00 micrograms/L should be used. Higher silicate concentrations (>200 micrograms/L) indicate that the higher ammonium criterion, 8.00 micrograms/L, should be used. The salinity/silicate method of choosing the appropriate ammonium criterion is valid anywhere within open coastal waters more than 2 meters from the shoreline, and eliminates problems of misinterpretation caused by attempting to relate shoreline freshwater discharge volumes, which mix to background levels within 500 – 1000 m from shore, to water quality between the reef edge and the 100-fathom contour line.

We have replaced the existing set of geometric means for ammonium (the "not to exceed 50%, 10% and 2%" values in the current rule) with the two proposed single-number standards (4.00 micrograms/L and 8.00 micrograms/L). Because ammonium concentrations are highly variable, the 10% and 2% values computed from small subsets of data from the sampling locations are large and inconsistent with the existing 10% and 2% values for nitrate and total nitrogen, and have been omitted from the proposed rule, at least until the WQS for nitrate and total nitrogen have been recomputed from the same data sets used for the ammonium analysis (Figure 4).

Use of two single dry-weather criteria should adequately account for variation over time and space when sampling efforts are confined to typical dry weather conditions.

The effect of biological activity in the water column and on the seafloor contributes to the range of variability seen in ammonium data sets. The general guideline should be to not sample near large schools of fish, and to expect higher ammonium values over coral reefs than over sand bottoms (see Brock, 2000 for a discussion of the impact of marine biota on ammonium concentrations).

Do the Proposed Criteria Exclude Locations with Anthropogenic Impacts on Ammonium Concentrations?

The two proposed ammonium criteria are based on the highest concentrations measured over the past ten years in "natural" coastal waters, defined as waters relatively unimpacted by anthropogenic activities, where water quality may reasonably be interpreted as representing baseline conditions. Sample means from many developed locations also meet the two proposed criteria (Table 1). Do these proposed criteria exclude sample means from areas known to be heavily impacted by polluted runoff? A review of Laws' data from beaches along the south coast of Oahu, and comparison with Dollar's data from Maui and West Hawaii shorelines, helps to answer this question.

Mean values for salinity, silicates, and ammonium from monthly samples collected 2-3 m offshore from 10 frequently used public beaches from Diamond Head to Barbers Point show ammonium concentrations ranging from 5.27 micrograms/L at Fort Kamehameha Beach to 13.60 micrograms/L at Ewa Beach. Mean ammonium concentrations were surprisingly stable within both low and high salinity category waters and across a wide range of silicate concentrations (Table 2). On the other hand, values of the same parameters in water samples collected by

Dollar at locations 1-2 m from the shoreline in West Hawaii and West Maui have mean ammonium concentrations ranging from 1.35 micrograms/L to 1.54 micrograms/L, about half that of the proposed high salinity category criterion, 4.00 micrograms/L (Table 2). Shoreline samples collected by Dollar at the western edge of Oneula Beach (Dollar's transect OE at Ewa Beach), had a mean ammonium concentration of 4.08 micrograms/L, less than that measured by Laws at Oneula Beach (10.99 micrograms/L) and below the low salinity category criterion of 8.00 micrograms/L.

On the basis of these limited data, it appears that ammonium concentrations very close to shore (1-2 m) are either consistently high, regardless of salinity and silicates, in areas receiving large anthropogenic nutrient subsidies from land (Laws' data), or consistently low, regardless of salinity and silicates, in less developed areas on the Ewa coastline and on West Maui and West Hawaii (Dollar's data). When the ammonium means for Laws' shoreline data are sorted into higher and lower salinity categories, the result is that 10 of the 11 locations exceed the appropriate ammonium criterion (the exception is Fort Kamehameha Beach); applying the same exercise to Dollar's shoreline data from the Ewa coastline, West Maui and West Hawaii results in inclusion of all sample means below the appropriate criterion.

The proposed ammonium criteria do exclude geometric mean ammonium concentrations for Waikiki beaches, as warranted by their proximity to highly developed watersheds, and include concentrations from parts of the Ewa coastline, and West Maui and West Hawaii beaches adjacent to less intensively developed areas, indicating that the proposed criteria are strict enough to exclude potential water quality-limited segments but not so strict as to exclude all developed areas. However, additional sampling is needed along beaches to provide coverage of the entire beach front and take into consideration location of storm drains and groundwater discharges, surf state, tidal stage, and the number and distribution of bathers, all of which may influence parameter values very close to shore.

Shoreline ammonium values can provide valuable information on the level of nutrient subsidies from land; if ammonium concentrations consistently exceed the applicable standard for the area, a strip of water along the shore can be defined as a water quality-limited segment, listed under CWA §303(d), and an ammonium TMDL prepared for the adjacent watershed.

Criteria for Design of Sampling Plans. Because ammonium values are highly variable over both space (the area sampled) and time (consecutive samples collected at a single station), the initial goal of the sampling effort must be to describe the background salinity/silicate pattern in the entire area of interest, not just close to the shoreline.

<u>Salinity/silicate pattern</u>: If the mean value of at least 15 salinity measurements distributed over the area of interest at least 2 m from the shoreline is >32.000 ppt and ≤34.400 ppt, then the ammonium criterion applicable to the area is equal to 8.00 micrograms/L (the 50 % "not to exceed" geometric mean value). If the mean salinity is >34.400 ppt the ammonium criterion applicable to the area is equal to 4.00 micrograms/L (the 50 % "not to exceed geometric mean value"). Corresponding silicate guidelines are ≥200 micrograms/L for the lower salinity category and <200 micrograms/L for the higher salinity category, and, as mentioned above, the

silicate categories are meant to be used as a “tiebreaker” for choosing the correct ammonium criterion to apply in cases where the mean sample salinity is at or very near 34.400 ppt. Sampling plans submitted to the Department of Health for review will be evaluated against these criteria:

1. For sampling purposes, “shoreline” means the location of the average wash of the waves at the time of sample collection. Paired salinity and silicate measurements ($N \geq 15$) should be taken at least 2 m offshore so that stable background levels are measured rather than the more variable condition close to shore where mixing is incomplete. Please note that salinity-silicate measurements need only be performed once for an area, during dry weather, and do not need to be repeated unless a major land use change affecting drainage in the area has occurred since the last set of measurements was taken.

   Salinity/silicate measurements are not necessary if the salinity category for the area has already been identified in this report or can be determined from other existing data sets (theoretical arguments will not be accepted; actual data are required for these determinations).

2. If you must prepare a salinity/silicate sampling plan in order to select the appropriate ammonium criterion for the area of the proposed project, the same stations may be used for ammonium sampling, or you may choose different stations, provided that the entire area to be affected by the project is covered. If the project includes the shoreline, identify the shoreline at the time of sampling as the line marking the average wash of the waves, then move seaward over a distance of at least 2 m before collecting your samples for ammonium determinations. Please measure the salinity corresponding to each ammonium sample.

3. If the sampling plan is required for a proposed coastal development, sample near the water surface (about 20 cm below the water surface) and near the bottom at 4 – 6 points along a transect perpendicular to shore out to either 500 m or 1000 m offshore. Results of this exercise will identify the area as conforming to either the 4.00 micrograms/L or the 8.00 micrograms/L ammonium criterion. If a beach area is being sampled, sample along the entire beach, not just at one end or in the middle. Run a sufficient number of transects to cover the entire frontage of the proposed development. If the area of interest is seaward of the reef, design a sampling plan that covers the entire area to be affected by the proposed project.

4. Taking two or three water samples near the shoreline will not be considered sufficient to evaluate areas of coastal waters adjacent to proposed developments or proposed permitted discharges; please ensure that your sampling protocols cover the entire area affected by the proposed project or discharge.

5. Please remember that single sample values should not be compared to the WQS; the WQS are geometric means that, because of underlying variability in surface water chemistry, are used to evaluate geometric means computed from data sets containing analytical results from at least 10 independent water samples from an area.

6. QA/QC: Please screen your water samples before analysis to remove any macroscopic biota, such as algal fragments, that may have been picked up during sampling.

Antidegradation Policy:

Advantages of promulgating the new ammonium criteria include: (1) derivation of criteria from statewide data sets containing measurements performed at low detection levels and high accuracy, and including data from waters adjacent to undeveloped areas; (2) a written description of how the proposed criteria were derived from these data sets; and (3) reduction of uncertainty in applying the criteria through demonstration that the proposed criteria are related to each of two distinct salinity patterns. Establishing two criteria for ammonium, rather than setting only one criterion at the 8.00 microgram/L level, will help to prevent eutrophic conditions from developing by limiting ammonium delivery into high salinity waters with naturally low ammonium levels and well-developed coral reefs. Because the proposed criteria are derived from data collected from natural coastal waters (Class AA waters), they reflect a range of historically stable conditions in waters relatively unimpacted by human activities and are appropriate for statewide application.

A survey of 15 dischargers required to measure ammonium concentrations in coastal waters as a requirement of NPDES permits with approved Zones of Mixing showed that all but one meet the lower proposed criterion, 4.00 ug/L (the exception is in an estuarine area). Existing dischargers will not receive a higher ceiling for ammonium discharges.

Disadvantages include an additional cost for establishing salinity/silicate patterns in selected areas; however, this cost need be incurred only once, unless major land use changes are proposed for an area. The cost of measuring salinity and silicates will be offset in part or completely by savings incurred by not having to evaluate coastal groundwater discharge volumes before deciding if “dry” condition or “wet” condition water quality standards are appropriate for the area of interest.

HAR Chapter 11-54-01.1, General policy of water quality antidegradation, currently states that high quality waters shall not be lowered in quality absent demonstration that the change supports important economic or social development, “…and will not interfere with or become injurious to any assigned uses made of, or presently in, those waters.” (see also the proposed amendment to the State's antidegradation policy.) Because the current ammonium criteria underestimate the range of ammonium concentrations in natural waters and are not based on site-specific data sets, protected and existing uses will not be not altered by recognition of the actual distribution of ammonium concentrations in different areas around the State.

ACKNOWLEDGMENTS

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Laws, Edward A. and David Ziemann (May, 1995). Ecosystem Response Study: Effect of Sewage Discharges and Stream Runoff on Phytoplankton Communities and Water Quality in Mamala Bay (Project MB-9). Prepared for the Mamala Bay Study Commission. P. 82.

Table 1. Summary of data used to derive the proposed new ammonium criteria. Data are arranged by rank order of salinity, with the open ocean approximate minimum value of 34.400 ppt (upper 31 m of the water column) used to separate the lower salinity category (proposed ammonium criterion = 8.00 micrograms/L) from the higher salinity category (proposed ammonium criterion = 4.00 micrograms/L).

LOCATION	DEV/UND	N (SAL>32.000 ppt)	TOTAL N	MEAN SALINITY (ppt)	MEAN SILICATE micrograms/L	MEAN AMMONIUM micrograms/L
Hanamaulu (Brock)	DEV	12	30	33.5097	214.32	6.11
Kaloko (Brock)	UND	49	59	33.7140	520.86	4.84
Waikoloa (Brock)	DEV	228	300	33.9439	456.85	4.57
Kailua-Kona (Dollar)	DEV	35	40	33.9462	232.06	4.36
Kauai (Brock)	DEV	25	30	33.9696	155.55	3.58
Puako (Dollar)	DEV	30	31	34.0356	271.22	1.66
Kiilae (Dollar)	UND	31	31	34.0554	178.64	1.74
Keahou (Dollar)	DEV	34	40	34.0596	218.37	1.53
Makalawena (Brock)	UND	23	27	34.1246	182.68	3.78
Kukio (Brock)	UND	152	191	34.1454	276.83	5.69
Mahinahina (Dollar)	DEV	52	52	34.2090	200.90	1.58
Alaeloa (Dollar)	DEV	51	52	34.2310	281.28	1.28
Hokukano (Brock)	UND	69	69	34.3840	176.94	4.03
ALOHA Station 2		3367	3367	34.4000	43.00	0.80
Ewa – Control (Dollar)	DEV	900	900	34.4100	209.61	1.92
Honokua Gulch (Dollar)	UND	36	36	34.4211	94.27	0.71
Ewa – West (Dollar)	DEV	900	900	34.4580	176.76	1.85
Ewa – East (Dollar)	DEV	900	900	34.5420	137.93	1.99
Ewa – Central (Dollar)	DEV	240	240	34.5530	146.72	2.59

Table 1 (continued).

LOCATION	DEV/UND	N (SAL>32.000 PPT)	TOTAL N	MEAN SALINITY (ppt)	MEAN SILICATE micrograms/L	MEAN AMMONIUM micrograms/L
Lahaina (Brock)	DEV	30	36	34.5600	91.68	1.14
Mala Wharf (Dollar)	DEV	50	51	34.5675	102.81	1.14
Honokowai (Dollar)	DEV	52	52	34.6008	94.88	0.94
Lanai (Brock)	DEV	347	347	34.6056	85.8	2.50
Lanai (Brock)	UND	220	220	34.6068	87.1	2.31
Kaanapali (Brock)	DEV	25	26	34.6469	104.96	2.91
Puamana (Dollar)	DEV	48	48	34.6745	80.44	1.50
Mahukona (Brock)	UND	17	17	34.7294	67.72	2.40
Atlantis Site (Brock)	DEV	12	12	34.8650	55.86	2.00
100-ft Hole, S. Oahu (Brock)	DEV	17	17	35.1153	40.49	2.06

Table 2. Geometric means for ammonium concentrations at beach stations in Mamala Bay, Oahu (Laws); Ewa, Oahu (Dollar) West Maui (Dollar); and West Hawaii (Dollar). Samples were collected by Laws (08/93-07/94) close to shore but at least 2 m from the shoreline at the time of sampling. Samples were collected by Dollar at 1 m from the shoreline [Ewa coastline (04/97-06/00); West Hawaii (02/94-12/94)] or at 2 m from the shoreline (West Maui; 01/93-06-94). Note that beaches fronting less developed or undeveloped coastlines have lower ammonium levels than those in more densely populated areas, such as Waikiki, Oahu, although this conclusion needs to be confirmed by collecting larger data sets on West Maui and West Hawaii beaches.

LOCATION	MEAN SALINITY (ppt)	MEAN SILICATE (ug/L)	MEAN NH4 (ug/L)	SAMPLE SIZE
OAHU (Laws)				
Diamond Head	34.48	54.97	6.55	12
Queen's Surf	34.54	55.02	6.56	12
Fort DeRussy	34.49	90.64	9.71	12
Ala Moana Beach Park	34.68	85.03	10.31	12
Sand Island	34.50	70.50	8.22	12
Keehi Lagoon	32.71	243.85	9.99	12
Fort Kamehameha	33.54	321.27	5.27	11
Ewa Beach	33.81	173.91	13.60	12
Oneula Beach	34.27	158.15	10.99	12
Barber's Point Beach	34.26	82.13	9.44	12
OAHU (Dollar)				
Ewa Marina (on transect O-E at west end of Oneula Beach)	34.392	270.38	4.08	11
WEST MAUI (Dollar)				
Alaeloa	33.933	637.28	1.51	3
Mahinahina	33.956	346.46	1.19	4
Honokowai	34.402	134.03	0.97	4
Mala Wharf	33.853	288.42	2.11	3
Puamana	34.089	171.91	2.13	4
WEST HAWAII (Dollar)				
Honokua Gulch	34.156	214.87	0.84	4
Puako	34.429	1993.13	1.40	1
Keahou	33.116	1180.76	5.18	1
Kiilae	33.673	550.24	1.52	4

APPENDIX A

In response to requests from EPA staff and others to delay amendment of the ammonium criteria for open coastal waters until all nutrient parameters have been analyzed and "brought back into proportion with each other," we undertook a quick analysis of nitrate and total nitrogen data from only the Lanai (undeveloped) and Kukio (undeveloped) site data, collected by Richard Brock, University of Hawaii, in order to determine if the pattern in the existing WQS would be preserved for the three nitrogen parameters measured by Dr. Brock. Data from these sites were used to set the proposed WQS for ammonium in open coastal waters. The methodology used for this analysis is the same as that reported for the ammonium analysis.

Island of Lanai (undeveloped sample sites); values are given in micrograms/liter

LANAI	**MEANG(50%)**	**MEANG(10%)**	**MEANG(2%)**
Total Nitrogen	99.32	156.06	228.20
Nitrate	1.89	11.79	21.34
Ammonium	4.00	24.21	51.66

Island of Hawaii (undeveloped sample sites at Kukio).

KUKIO	**MEANG(50%)**	**MEANG(10%)**	**MEANG(2%)**
Total Nitrogen	116.43	220.50	307.63
Nitrate	14.43	179.48	6500.49
Ammonium	8.00	32.71	258.74

<u>Lanai results (higher salinity category waters):</u>

1. Note that ammonium concentrations exceed nitrate concentrations in the same samples. Because these are high salinity waters, with very little fresh water input from land, the most likely explanation is that there is a high rate of ammonium regeneration by benthic (reef) and water column organisms (fish). See Brock & Kam (April, 2000) for a discussion of the effects of biological metabolism of ammonium concentrations in coastal waters).
2. With the exception of ammonium, total nitrogen and nitrate geometric mean concentrations meet either the wet or dry WQS (existing) for open coastal waters, with total nitrogen meeting the "dry" criteria and nitrate meeting the "dry" criteria at the 50% level, and the "wet" criteria at the 10% and 2% levels.

<u>Kukio results (lower salinity category waters):</u>

1. Note that total nitrogen meets the existing "wet" WQS, but nitrate and ammonium exceed the corresponding WQS.

2. At the 2% level, geometric mean concentrations for the inorganic ions either exceed (nitrate) or approach (ammonium) the mean total nitrogen concentration.

Although geometric mean concentrations for total nitrogen meet either the existing "dry" WQS (Lanai) or existing "wet" WQS (Kukio), concentrations of the inorganic ions, especially ammonium, are elevated as a function of local salinity/silicate regimes and probably, in the case of ammonium, biological metabolism in Hawaii's diverse reef communities. Additional sample collection from the windward sides of islands is necessary before criteria for nutrients other than ammonium can be proposed for amendment, but results tabulated above demonstrate that proportions of nutrients measured in the same samples collected from relatively unpolluted nearshore coastal waters on leeward sides of islands are not consistent across at least two islands of differing geological ages and fresh water discharge characteristics, and that at least the 2% levels in the current WQS tables are best deleted to avoid high variability at this end of the scale.

By promulgating the ammonium amendment now, we can provide a data-based WQS for ammonium, the form of nitrogen most out of alignment with existing WQS, and then carry out the same process for nitrate and total nitrogen, which, at least on the leeward sides of islands, are present in concentrations similar to those given in the existing WQS. Data for phosphorus and chlorophyll a will also be analyzed, and the WQS adjusted as needed.

Table 1. Summary of data used to derive the proposed new ammonium criteria. Data are arranged by rank order of salinity, with the open ocean approximate minimum value of 34.400 ppt (upper 31 m of the water column) used to separate the lower salinity category (proposed ammonium criterion = 8.00 micrograms/L) from the higher salinity category (proposed ammonium criterion = 4.00 micrograms/L).

LOCATION	DEV/UND	N (SAL>32.000 ppt)	TOTAL N	MEAN SALINITY (ppt)	MEAN SILICATE micrograms/L	MEAN AMMONIUM micrograms/L
Hanamaulu (Brock)	DEV	12	30	33.5097	214.32	6.11
Kaloko (Brock)	UND	49	59	33.7140	520.86	4.84
Waikoloa (Brock)	DEV	228	300	33.9439	456.85	4.57
Kailua-Kona (Dollar)	DEV	35	40	33.9462	232.06	4.36
Kauai (Brock)	DEV	25	30	33.9696	155.55	3.58
Puako (Dollar)	DEV	30	31	34.0356	271.22	1.66
Kiilae (Dollar)	UND	31	31	34.0554	178.64	1.74
Keahou (Dollar)	DEV	34	40	34.0596	218.37	1.53
Makalawena (Brock)	UND	23	27	34.1246	182.68	3.78
Kukio (Brock)	UND	152	191	34.1454	276.83	5.69
Mahinahina (Dollar)	DEV	52	52	34.2090	200.90	1.58
Alaeloa (Dollar)	DEV	51	52	34.2310	281.28	1.28
Hokukano (Brock)	UND	69	69	34.3840	176.94	4.03
ALOHA Station 2		3367	3367	34.4000	43.00	0.80
Ewa – Control (Dollar)	DEV	900	900	34.4100	209.61	1.92
Honokua Gulch (Dollar)	UND	36	36	34.4211	94.27	0.71
Ewa – West (Dollar)	DEV	900	900	34.4580	176.76	1.85
Ewa – East (Dollar)	DEV	900	900	34.5420	137.93	1.99
Ewa – Central (Dollar)	DEV	240	240	34.5530	146.72	2.59

Table 1 (continued).

LOCATION	DEV/UND	N (SAL>32.000 PPT)	TOTAL N	MEAN SALINITY (ppt)	MEAN SILICATE micrograms/L	MEAN AMMONIUM micrograms/L
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Keahou	33.116	1180.76	5.18	1
Kiilae	33.673	550.24	1.52	4

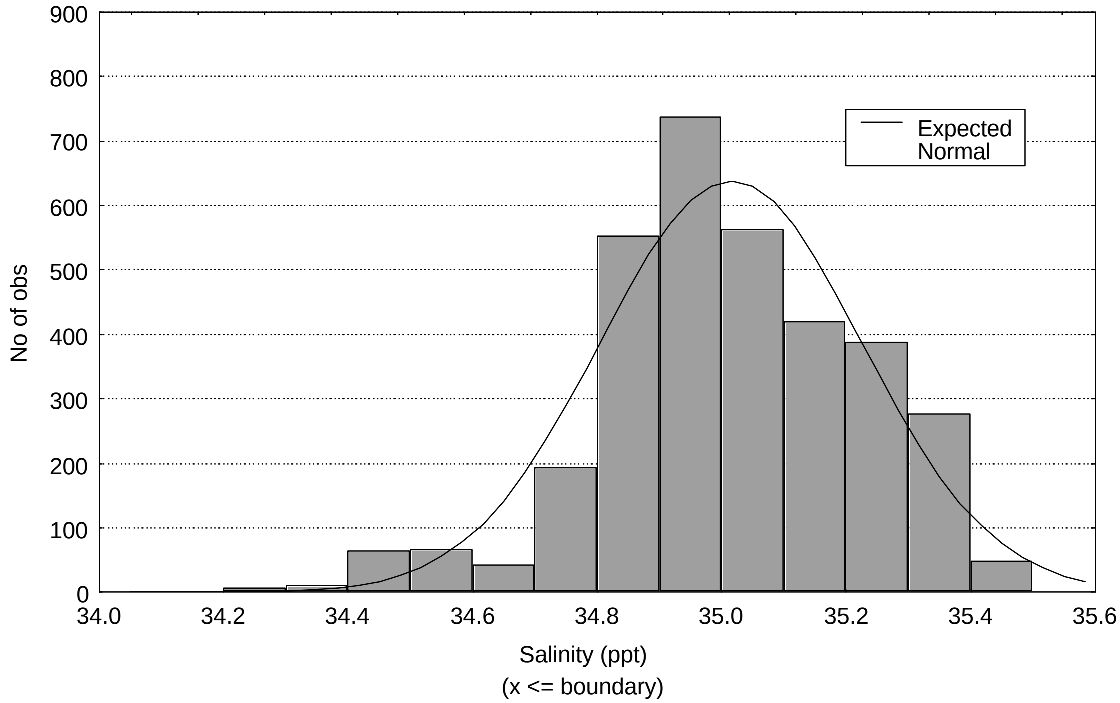


Figure 1. Distribution of salinity bottle data (n = 3367) in upper 31 meters of the water column at ALOHA Station 2; data collected from October 1, 1988 to December 31, 1999 at UH/HOTS deep ocean station about 100 km northeast of Oahu.

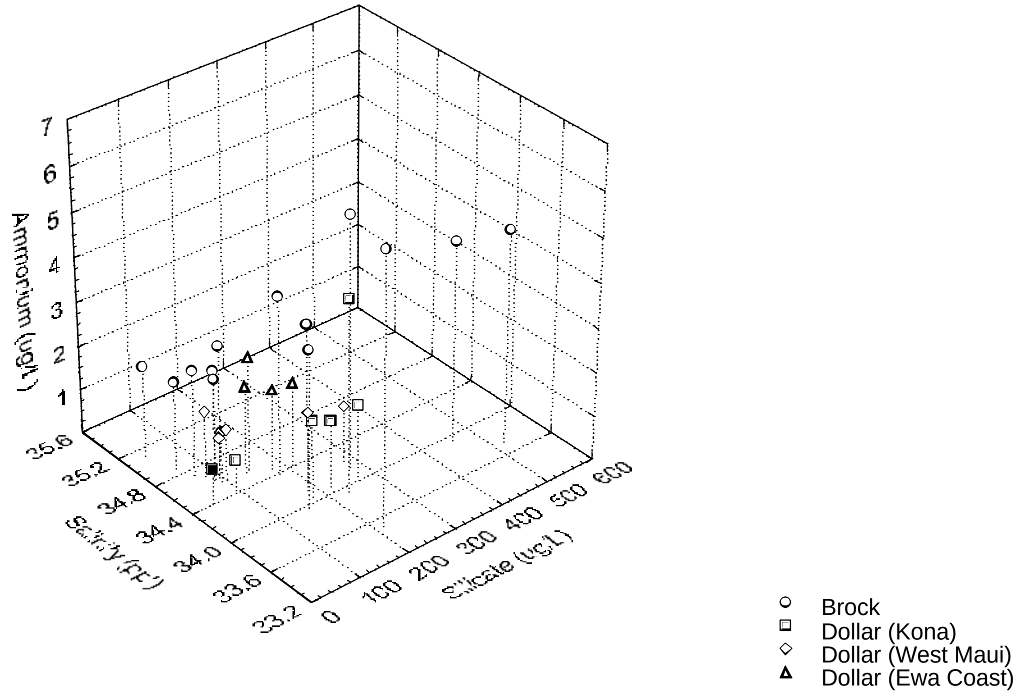


Figure 2. Distribution of mean salinity, silicate and ammonium values across the 28 locations sampled. The solid square on the middle left side of the graph represents offshore values for silicate and ammonium, shown at the lower boundary for offshore salinities, 34.400 ppt. Note that higher ammonium mean values tend to be associated with lower salinities and higher silicate values.

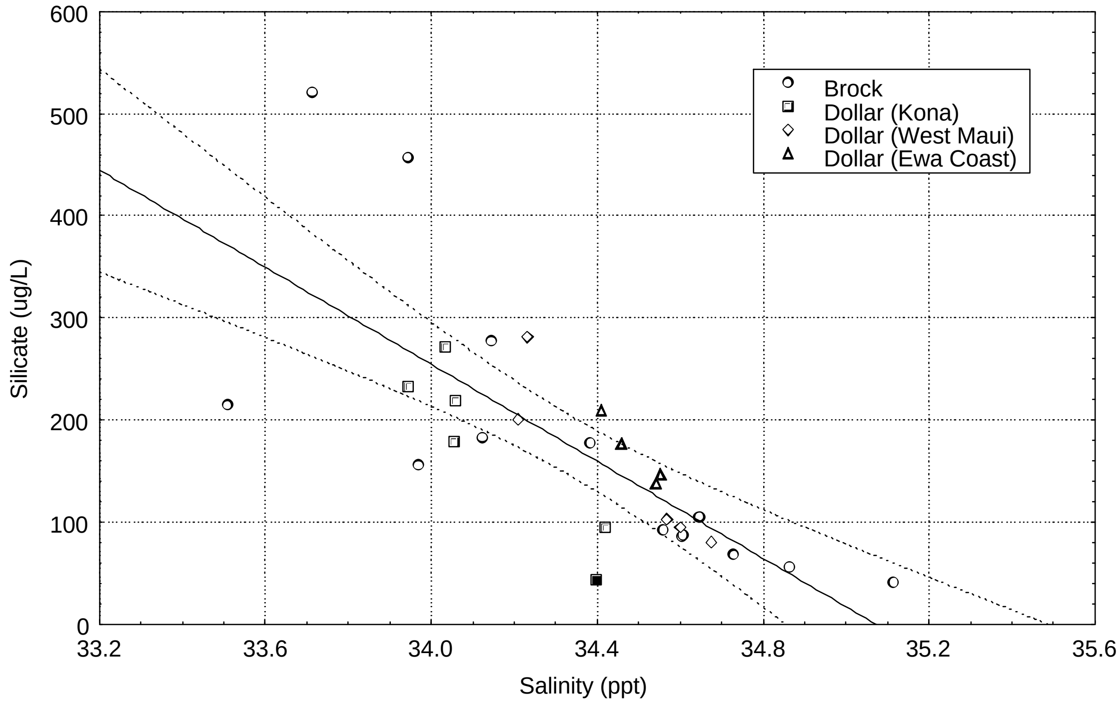


Figure 3. Relationship between salinity and silicate across the 28 sampled locations; r = -0.76. The solid square at the lower midpoint of the graph represents offshore conditions.

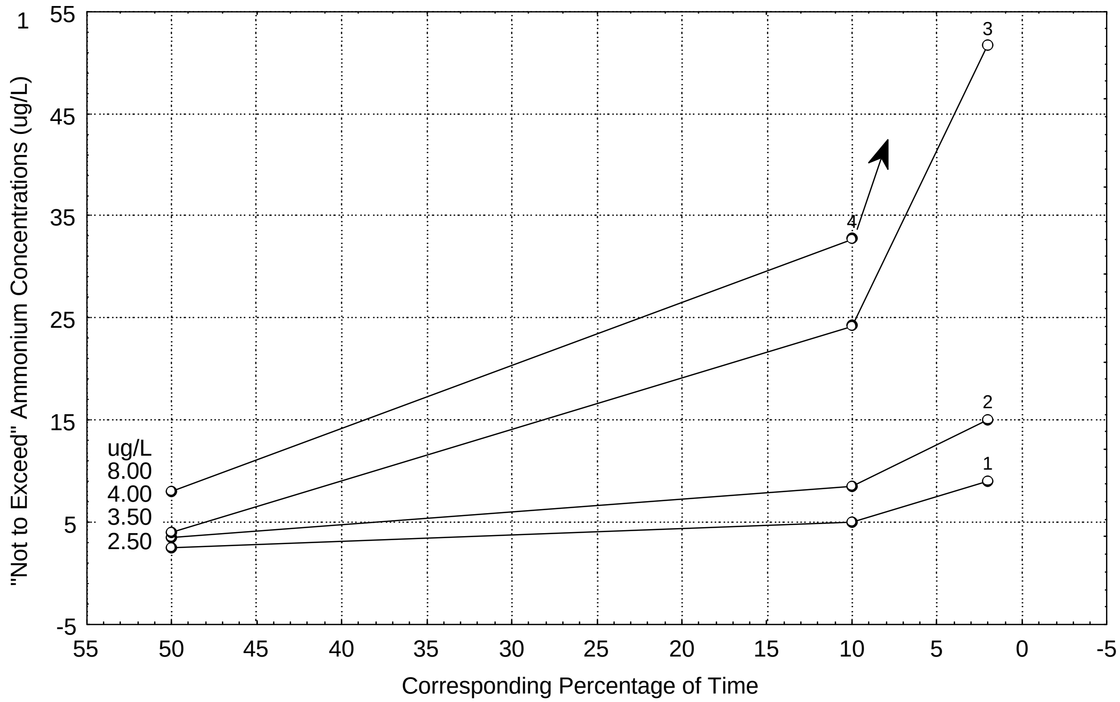


Figure 4. Ammonium criteria: (1) existing "dry" criteria [11-54-06(b)(3); April 4, 2000 edition of the rule]; (2) existing "wet" criteria; (3) proposed "higher salinity category" criterion (only the "50% or the time" value, 4.00 micrograms/L, is proposed for inclusion in the rule); and (4) proposed "lower salinity category" criterion (only the "50% of the time" value, 8.00 micrograms/L, is proposed for inclusion in the rule. The "2% of the time" value on line 4 (258.74 micrograms/L), was omitted to avoid scale compression at the "50%" level.

Figure 5. Location of water quality monitoring stations (Brock). 5a. Island of Kauai. 5b. Island of Maui. 5c. Island of Oahu. 5d. Island of Hawaii, Anaehoomalu area. 5e. Island of Hawaii, Keahole area. 5f. Island of Hawaii, Kealakekua area. 5g. Island of Hawaii, Mahukona area. 5h. Island of Hawaii, Makalawena area. 5i,j,k. Island of Lanai

Island of Kauai Ammonium Monitoring Stations

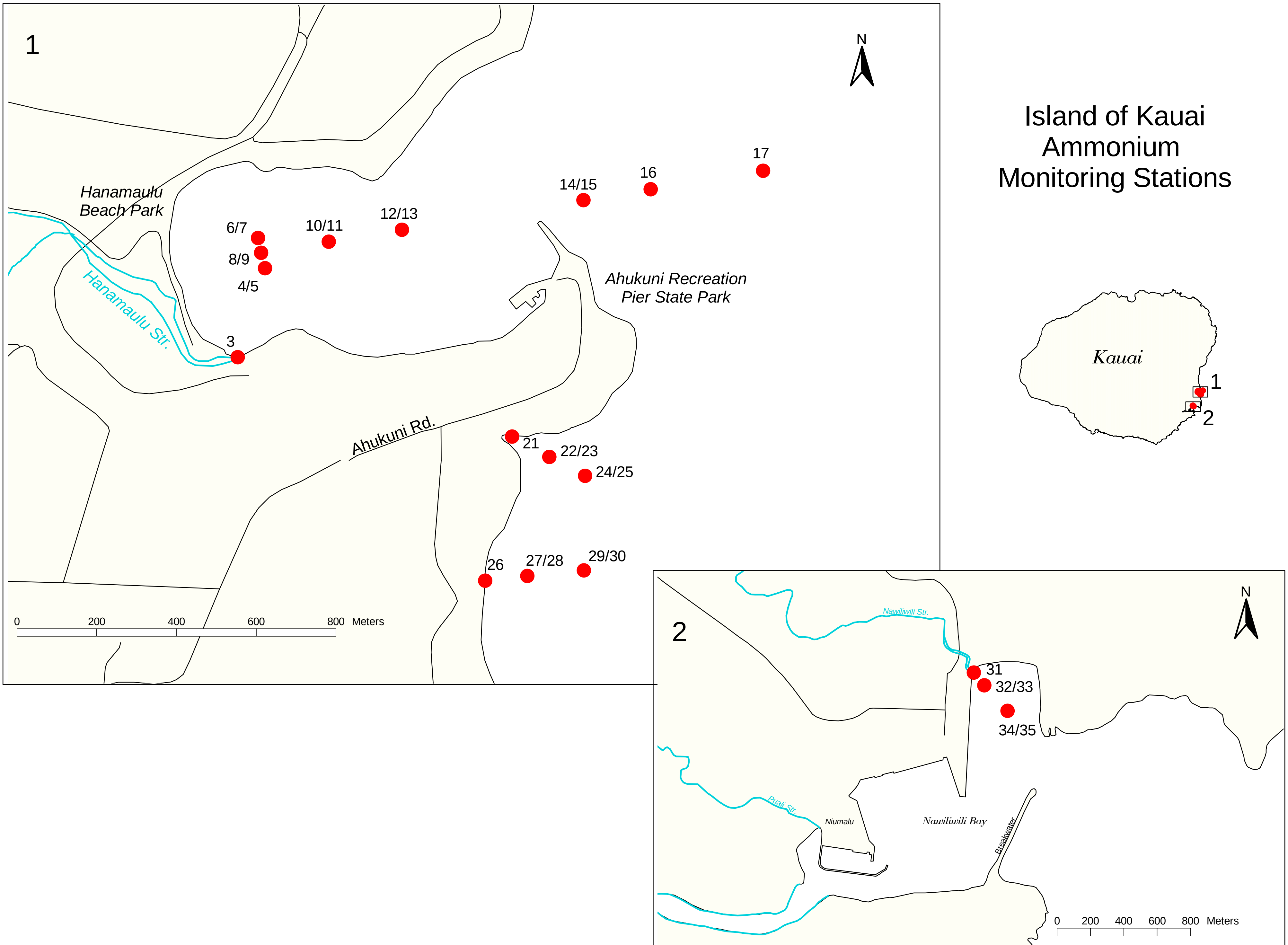


Figure 5a.

Department of Health 12/2000

West Maui Ammonium Monitoring Stations

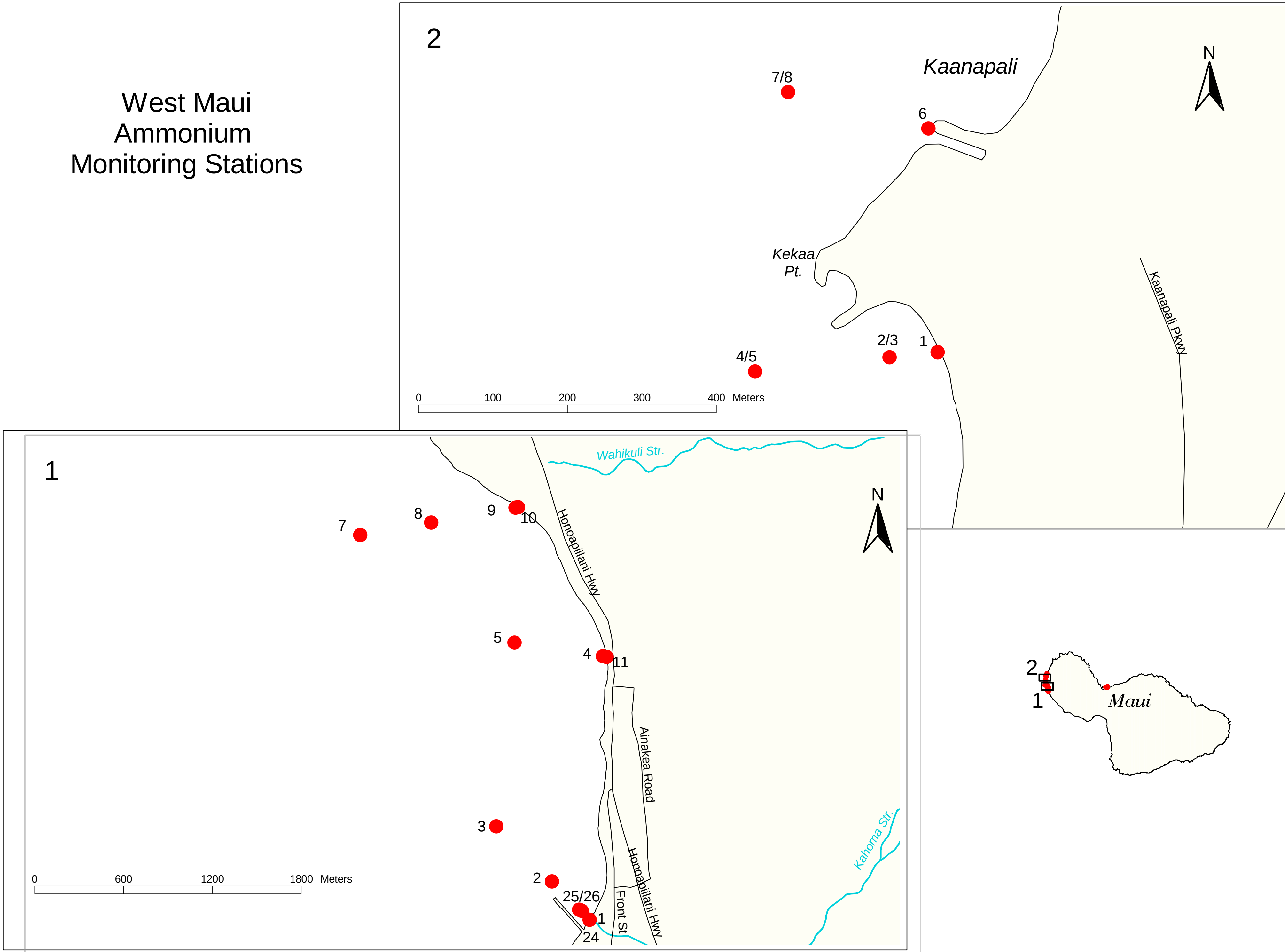


Figure 5b.

Department of Health 11/2000

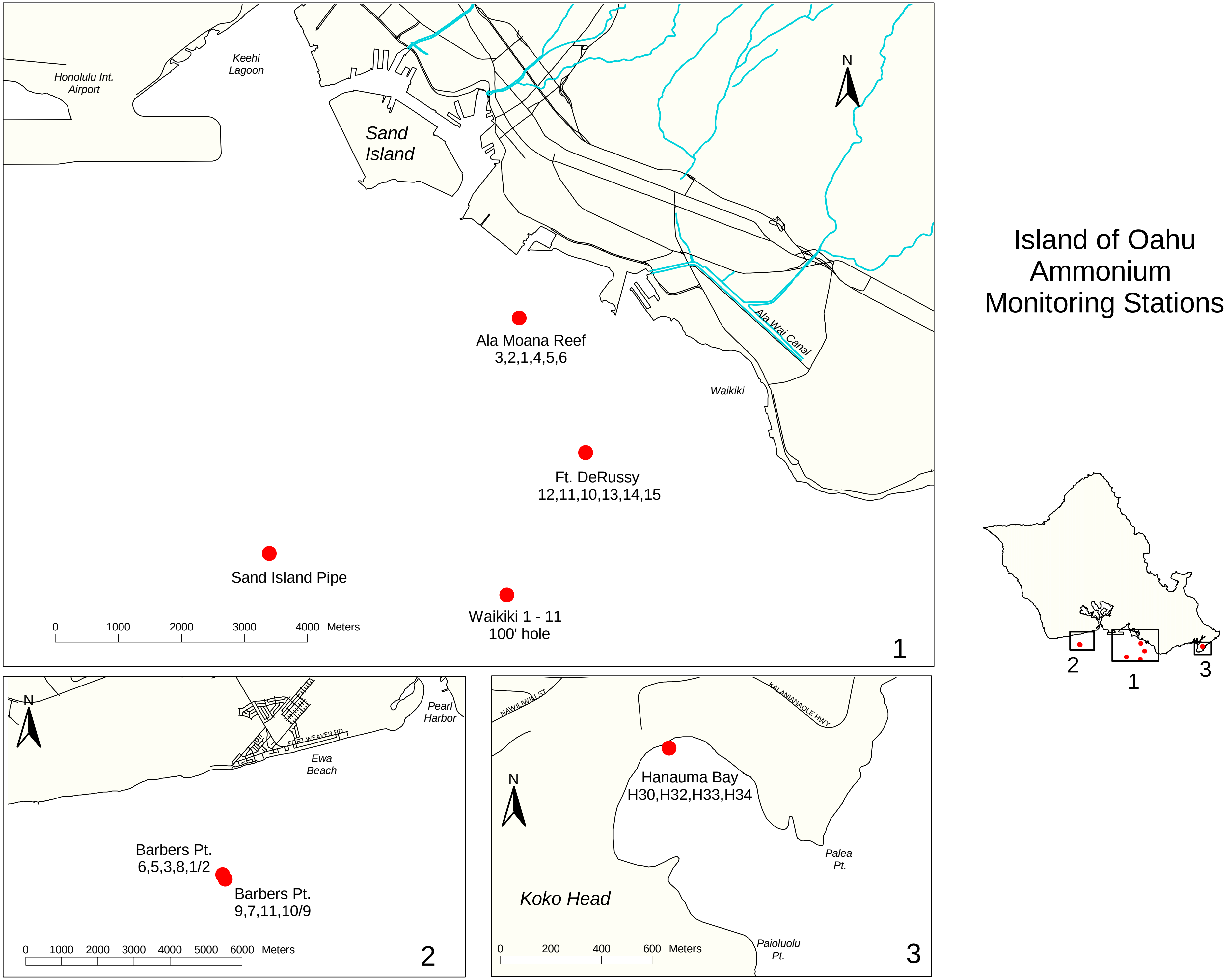
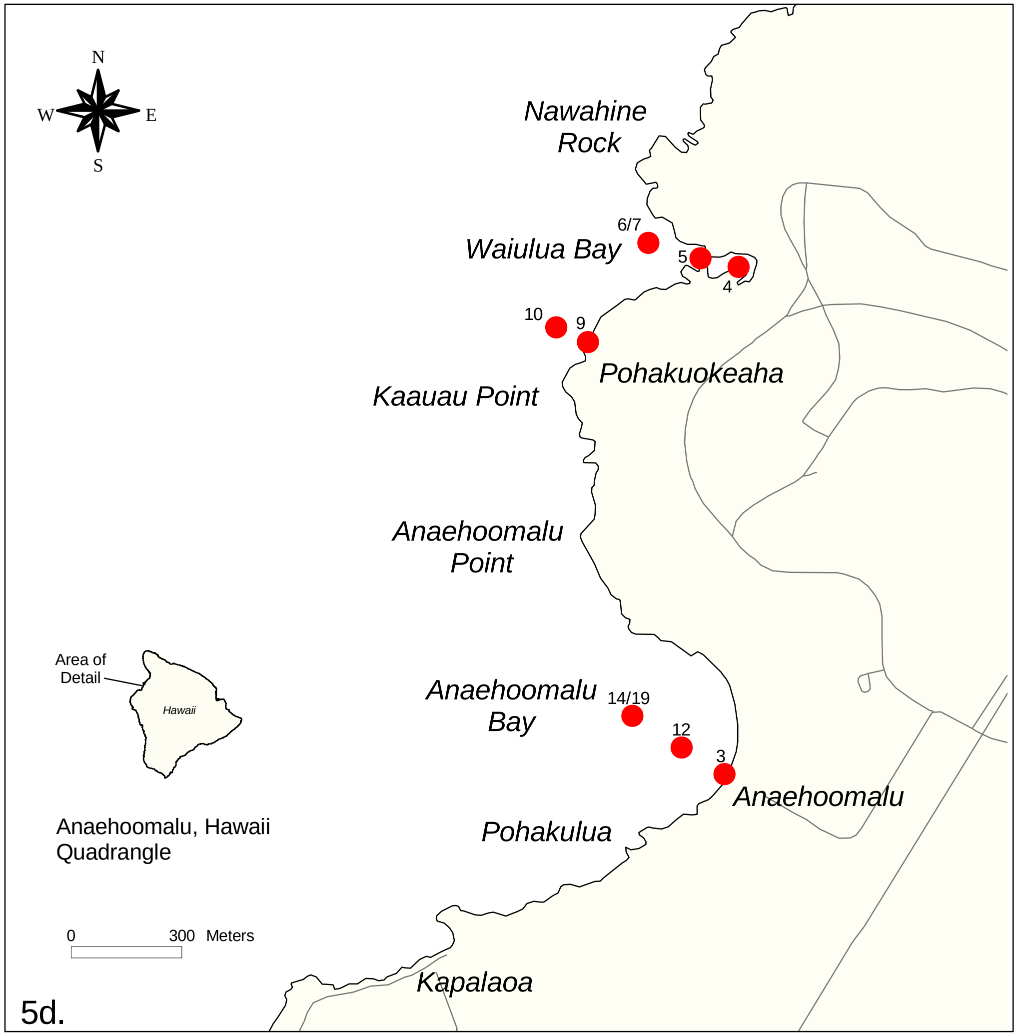
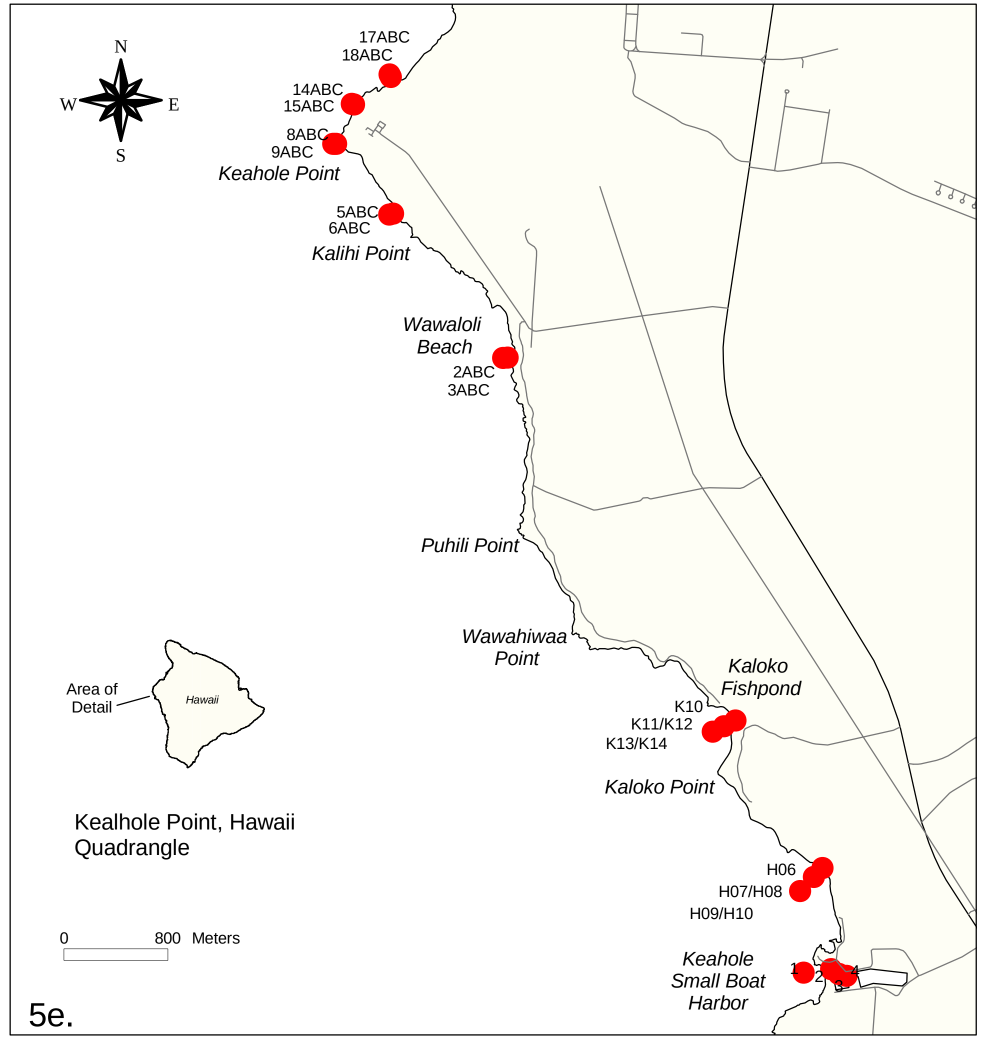


Figure 5c.

Department of Health 12/2000





Island of Hawaii
Ammonium Monitoring Stations

Figures 5d. and 5e.

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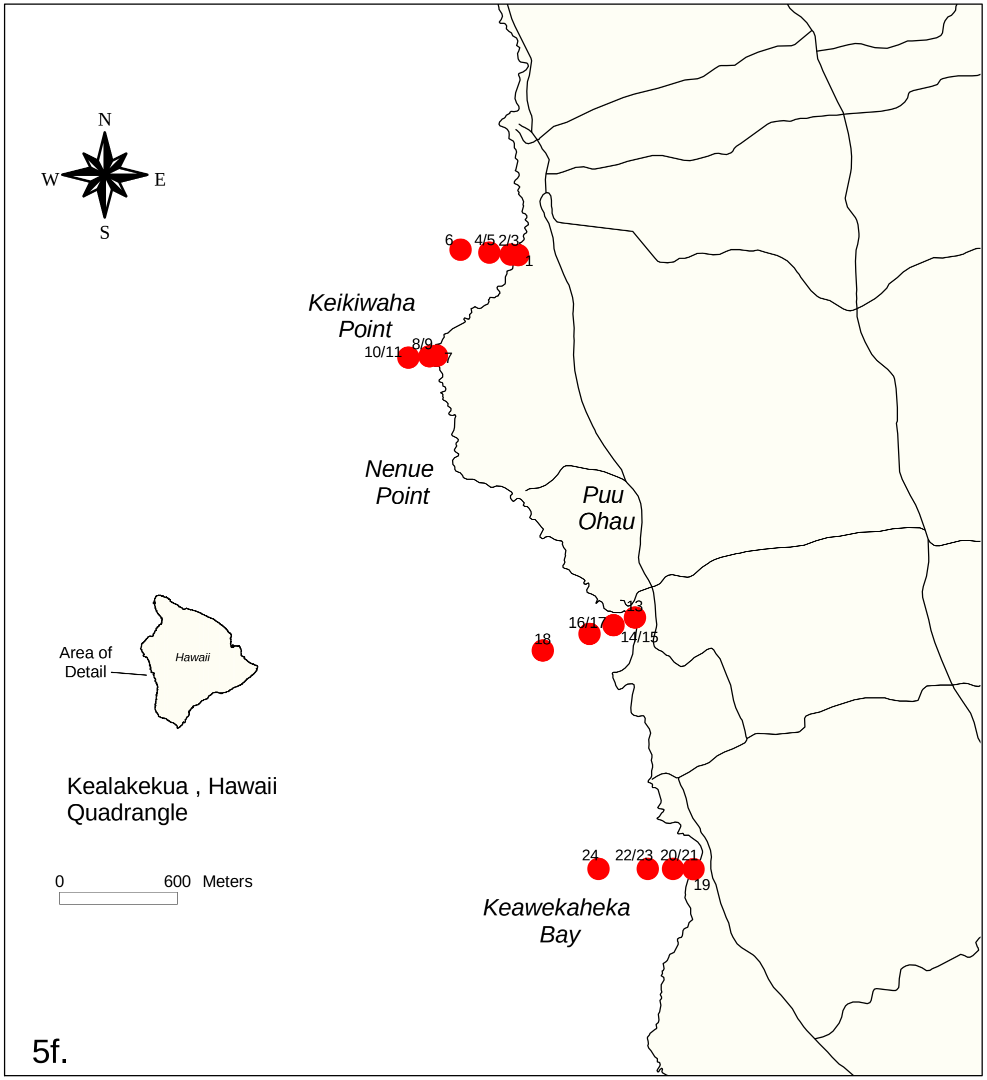

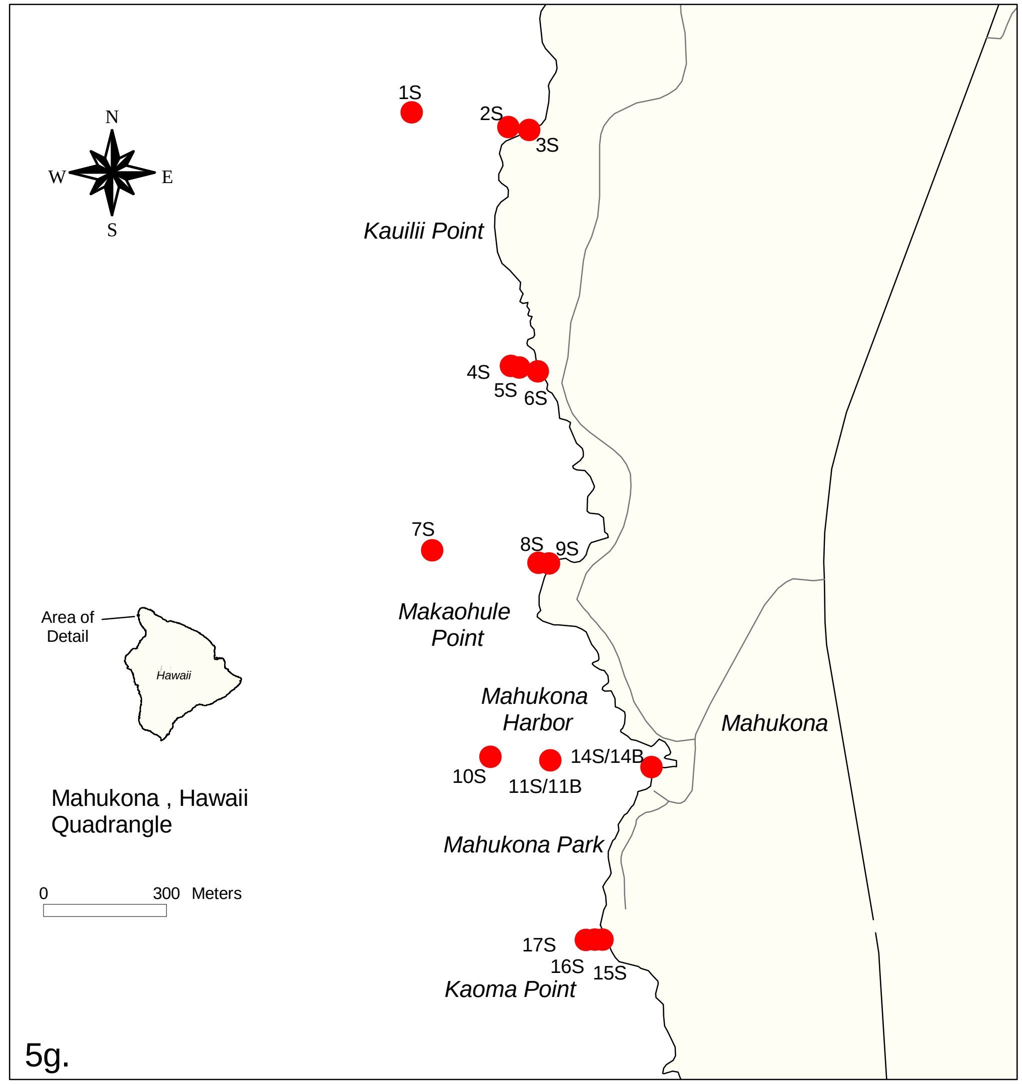

Island of Hawaii
Ammonium Monitoring Stations

Figures 5f. & 5g.

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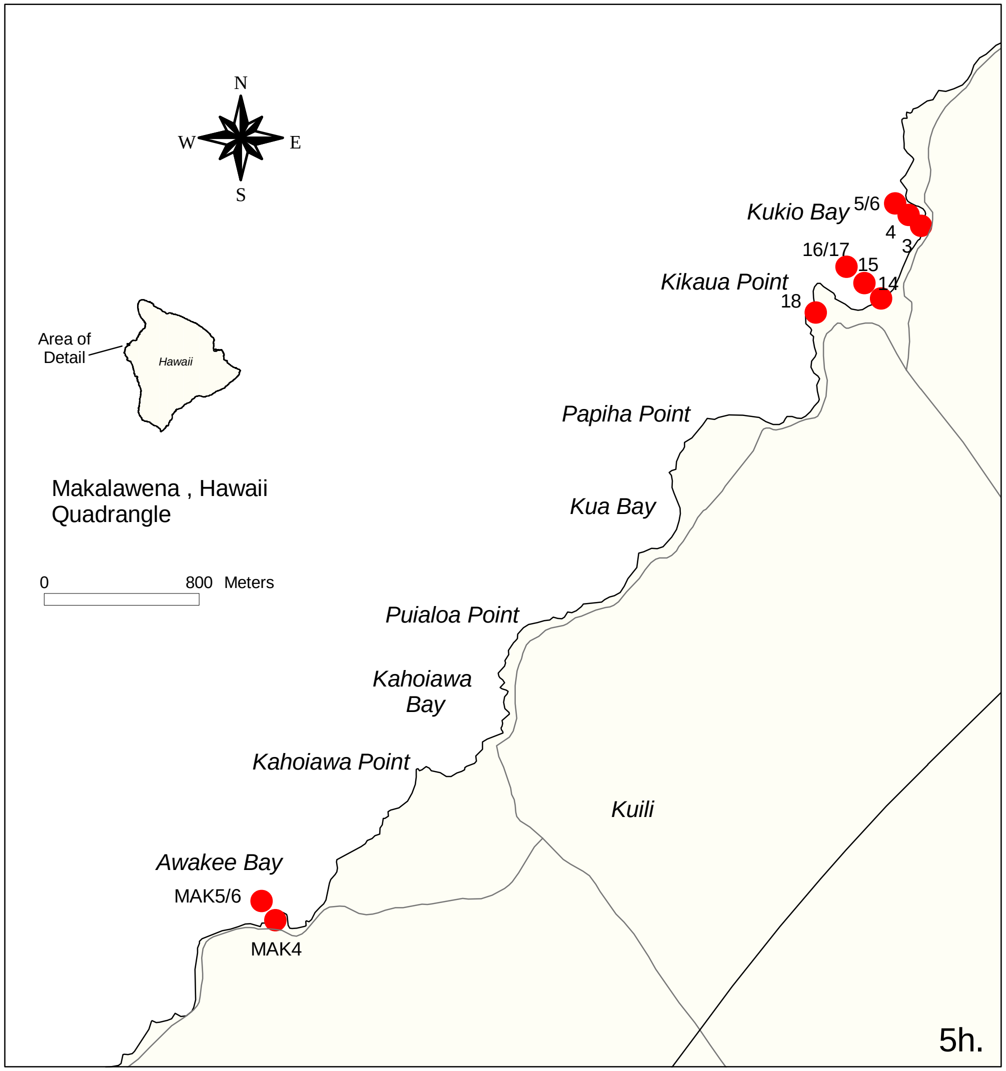
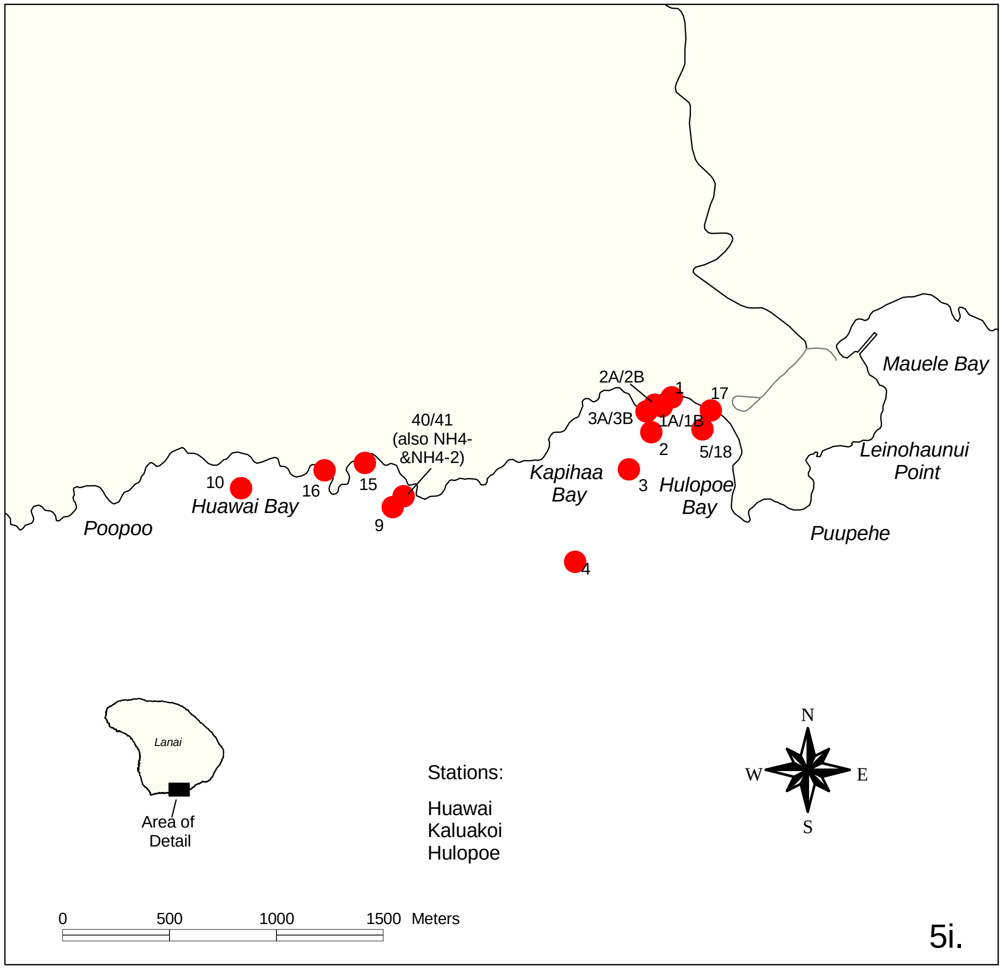
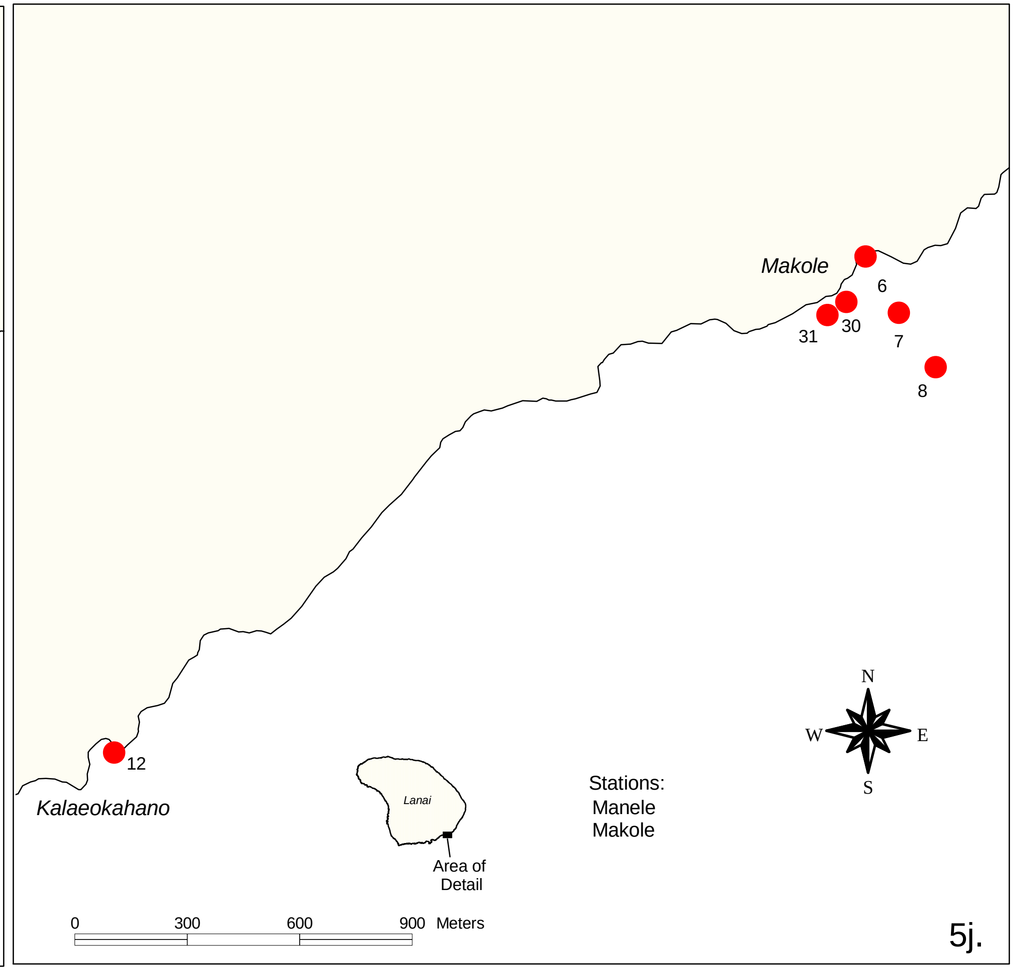


Island of Hawaii
Ammonium Monitoring Stations

Figure 5h.

Department of Health 12/2000

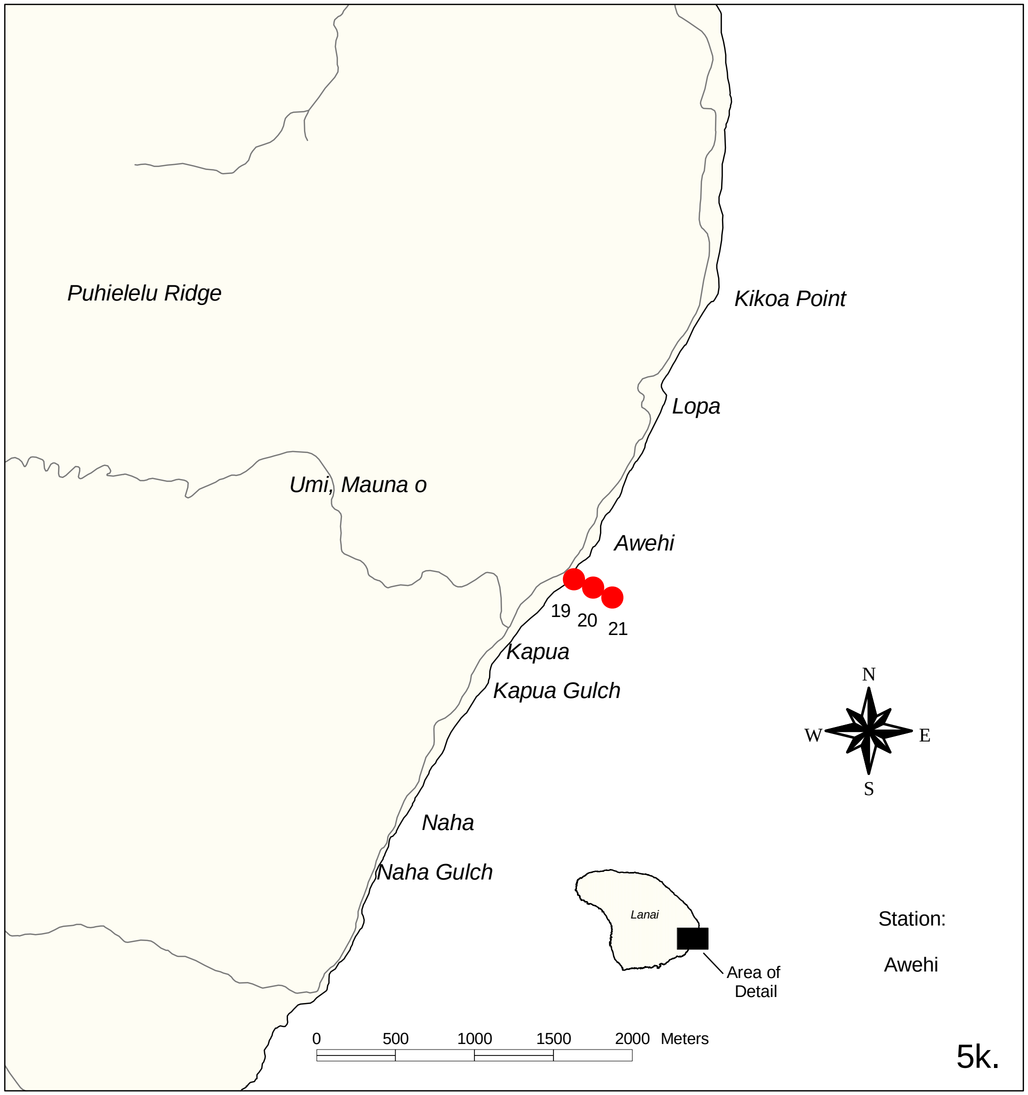




Island of Lanai
Ammonium Monitoring Stations

Figures 5i. & 5j.

Department of Health 12/2000



Island of Lanai
Ammonium Monitoring Stations

Figure 5k.

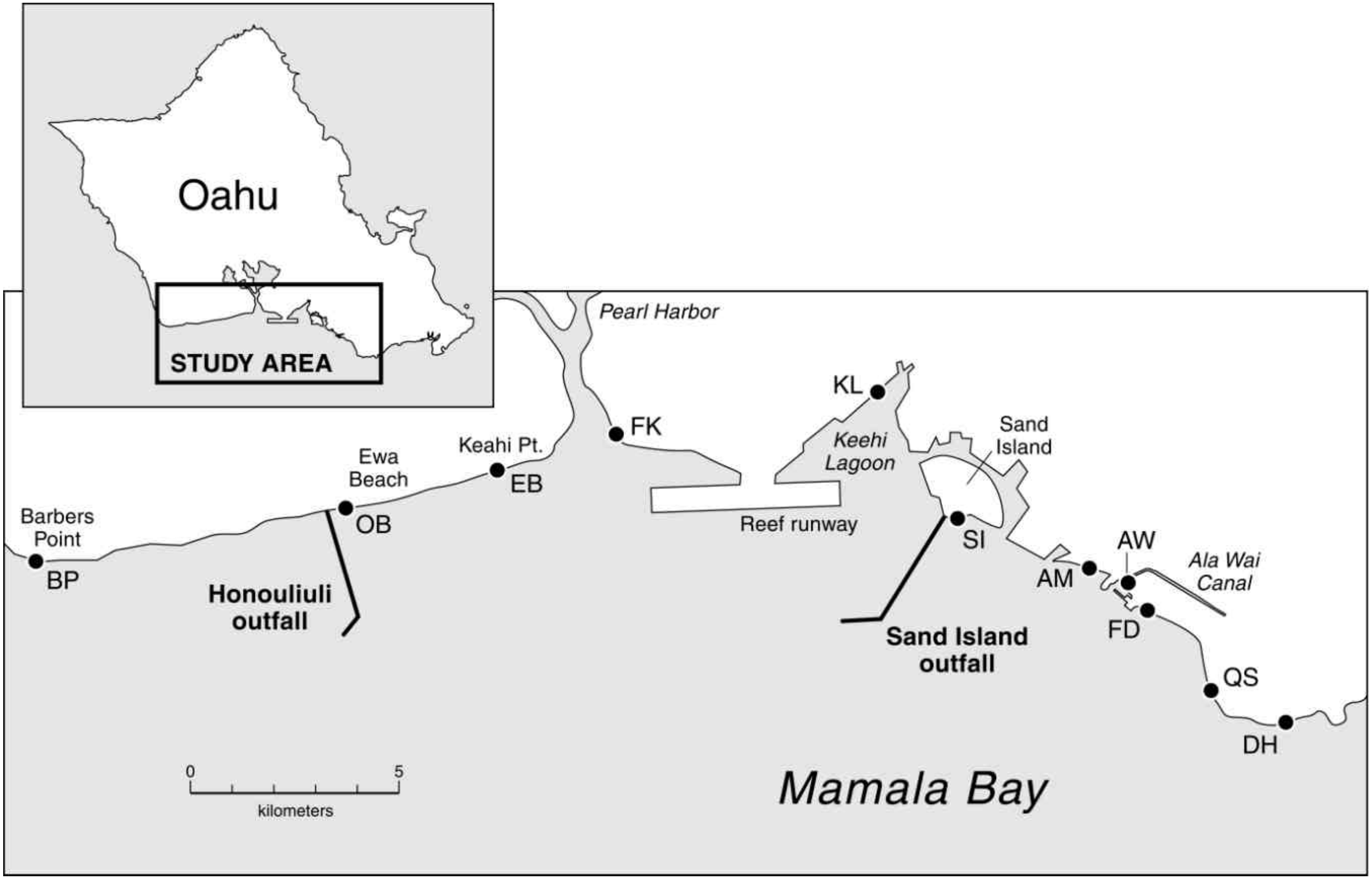


Figure 6. Sampling stations in Mamala Bay, island of Oahu (Laws & Ziemann, 1995).

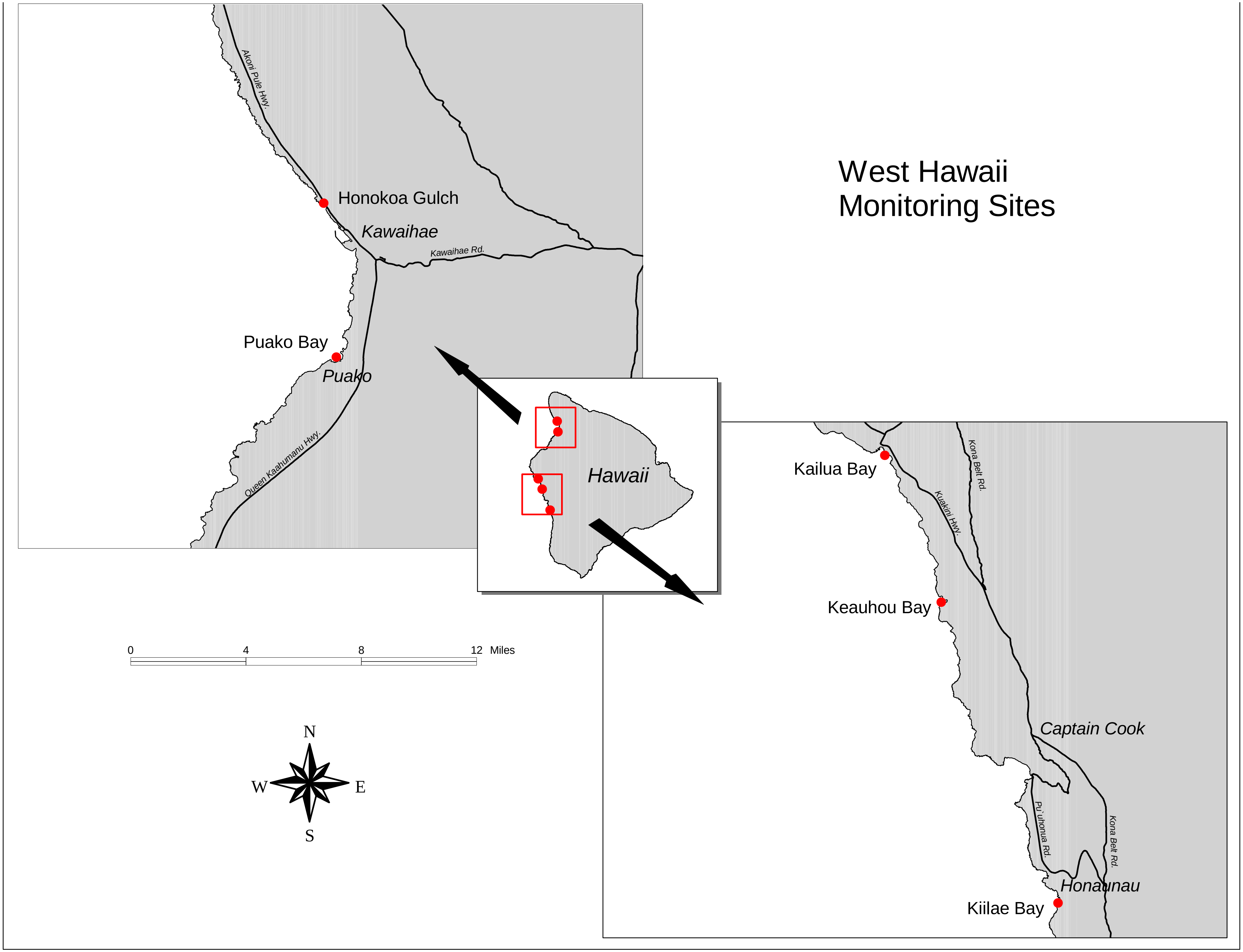


Figure 7. Sampling Stations on the Kona (west) Coast of the Island of Hawaii (Dollar, Brock, and Smith; 1996).

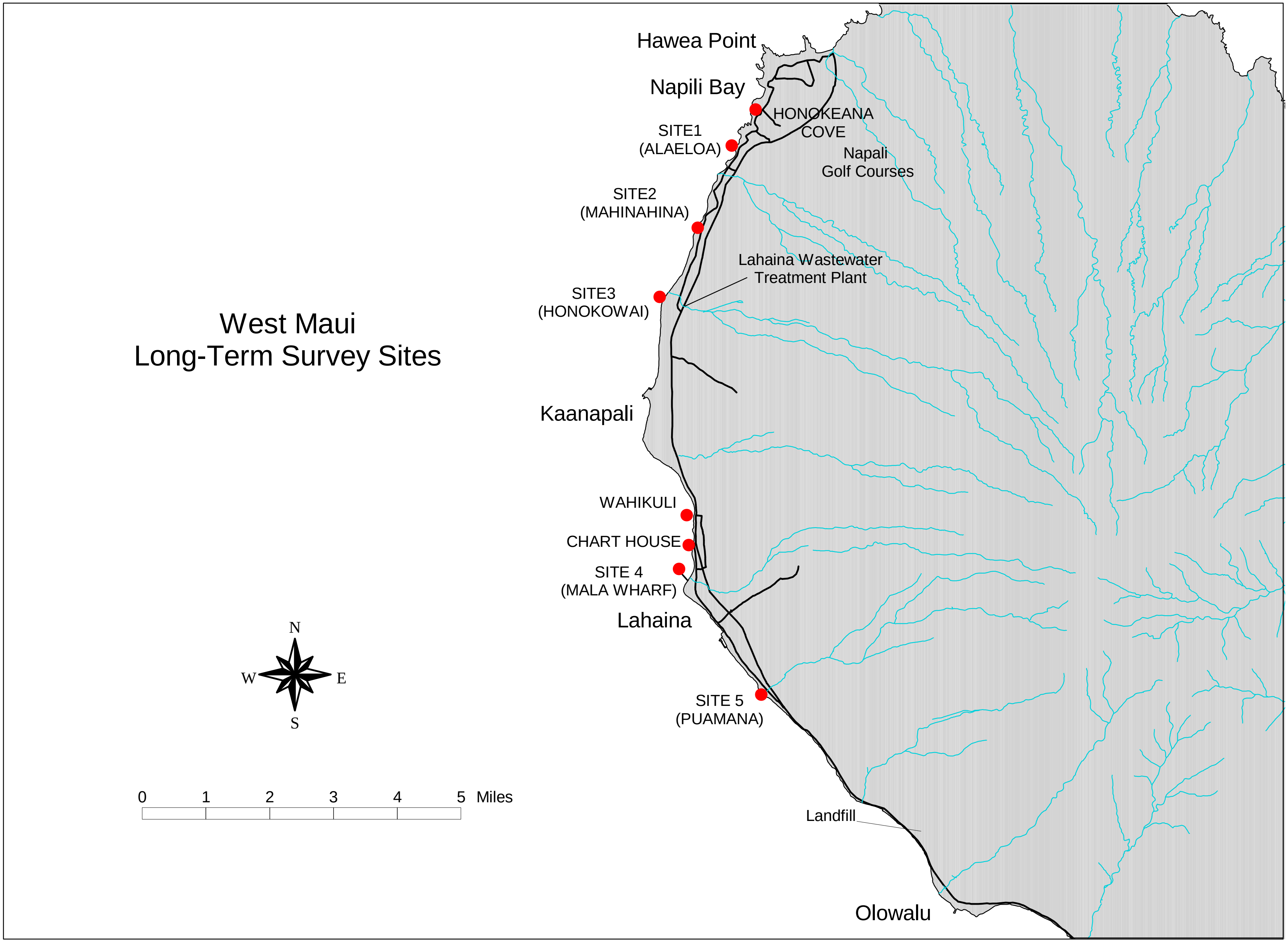


Figure 8. Sampling stations on the coastline of West Maui, Lahaina District (Dollar and Andrews; 1997).